STUDY ON THE EFFECT OF DIFFERENT PREPARATION METHODS OF DOPE SOLUTION ON DEVELOPMENT OF POLYETHERSULFONE MMMs FOR O_2/N_2 SEPARATION

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ABSTRACT

The developments in inorganic particles insertion in the polymeric membrane called as mixed matrix membrane (MMMs) have been fundamental to the advances in membranes gas separation technology. The objectives of this study are to develop high performance asymmetric polyethersulfone (PES) mixed matrix membranes for oxygen (O_2) and nitrogen (N_2) gas separation by manipulating three different methods preparation of dope solution. The asymmetric flat sheet membranes were fabricated via dry/wet phase inversion technique. The polymer solution consists of polyethersulfone as a polymer, 1-methyl-2-pyrrolidone (NMP) as a solvent and zeolite 5A as inorganic particles. The modified zeolite was prepared by treating the zeolite 5A with 3-Aminopropyl-Trimethoxysilane (APTMOS) to allow PES chain merged on the zeolite surface. The prepared membrane was coated using Polydimethyl siloxane and n-hexane in order to get the defect free membranes. The performance of membranes was examined using oxygen and nitrogen as test gases. The surface morphology of the prepared membrane was identified using scanning electron microscopy (SEM). The result shows that the best performance for O_2/N_2 separation was using second method named homogeneous polymeric solution formation where the selectivity was 4.50 while the lowest selectivity is for the third method which is 0.96. The optimum pressure was found at 3 bars. Therefore, it can concluded that by manipulating the different methods of dope solution preparation will influenced on gas separation performances and characteristics.

ABSTRAK

Pembangunan dalam penambahan bahan bukan organic di dalam membran polimer ataupun dikenali sebagai membran campuran matrik (MMMs) telah menjadi asas kemajuan dalam teknologi pemisahan gas melalui membran. Tujuan kajian ini dilakukan adalah untuk menghasilkan polyethersulfone (PES) membran tidak simetri yang berkualiti tinggi untuk pemisahan gas oksigen (O_2) dan nitrogen (N_2) dengan menggunakan tiga cara penyediaan campuran yang berbeza. Membran tidak simetri yang rata dihasilkan melalui kaedah proses fasa balikan kering/basah. Campuran polimer mengandungi polyethersulfone sebagai polimer, 1-methyl-2-pyrrolidone (NMP) sebagai bahan pelarut dan zeolit 5A sebagai bahan bukan organik. Pengubahsuaian terhadap zeolit dilakukan dengan menggunakan 3-Aminopropyl-Trimethoxysilane (APTMOS) untuk meningkatkan keserasian antara zeolit dan polimer. Membran yang terhasil akan disalut dengan silikon dan n-Heksana untuk tujuan mengurangkan kecacatan pada permukaan membran. Membran yang terhasil diuji mengunakan gas O_2 dan gas N_2 sebagai gas ujian. Imej permukaan serta keratan rentas membran yang terhasil dilakukan dengan menggunakan Mikroskop Pengimbas Elektron (SEM). Keputusan kajian menunjukkan prestasi pemisahan O_2 /N_2 yang terbaik adalah dengan menggunakan cara yang kedua iaitu campuran polimer sekata dengan nilai kadar pemilihan gas adalah4.50 manakala kadar pemilihan gas terendah adalah dengan menggunakan cara ketiga iaitu sebanyak 0.96. Tekanan optima adalah pada 3 bar. Dapat dibuktikan disini bahawa penggunaan cara penyediaaan campuran cecair yang berbeza mempengaruhi kadar pemisahan gas dan ciri-cirinya.

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LIST OF SYMBOLS

P	Overall permeability
α	Selectivity (Unitless)
Q	Flow rate of gas species (cm3/s)
A	Area of membrane (cm2)
ΔP	Pressure difference across membrane (cm Hg)
M	Charge balancing cation
n	cation valence
w	Moles of water contained in the zeolitic voids
μm	Micrometer
cm	Centimeter
%	Percentage
g	Gram
(P/*l*)	Pressure Normalized Flux (cm3 (STP)/ cm2. s. cmHg)
s	time in second
mmHg	millimeter mercury

LIST OF ABBREVIATIONS

CO_2	Carbon Dioxide
H_2	Hydrogen
H_2S	Acid gas
MMMs	Mixed Matrix Membranes
O_2	Oxygen
N_2	Nitrogen
SEM	Scanning Electron Microscopic
H_2O	Water
PES	Polyethersulfone
NMP	1-methyl-2-pyrrolidone
APTMOS	3-aminopropyl-trmethoxysilane
PDMS	Polydimethyl siloxane
EtOH	Ethanol solution
GPU	Gas Permeation Unit
Wt%	Weight percentage
℃	Degree celcius
STP	Standard pressure and temperature
Tg	Glass temperature

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CHAPTER 1

INTRODUCTION

1.0 Research Background

Membrane separate two phases of various chemical and transport them in a selective manner. The separation of mixtures of gases objective is to performed to obtain one or more constituents in pure form. There are many applications either large or small scale and only can be achieved by some methods based on different physical and chemical properties of the substances (Ravanchi *et al*., 2007).

Membrane process has certain advantages compare to the other separation technologies such as no specific chemical knowledge, minimize waste disposal costs, appreciable energy savings, reducing process materials requirements, compactness and light in weigh, low labor intensity, low cost and modular design permitting easy expansion to partial capacity (Ravanchi *et al*., 2007).

In gas separation technology, membrane has a wide range application include the permeation process through membrane. Permeation process becomes one of the fastest growing in the gas separation technology. The most widely used materials for gas separation are polymer. The limitation on the trade-off between permeability and selectivity influence the expanding application of membrane based gas separation in term of energy and capital cost (Li *et al*., 2008). The difference in permeability is resulted from diffusivity difference and from the physicochemical interactions between polymer matrix.

To overcome the limitation in the membrane gas separation, mixed matrix membranes have been marked as an alternative approach to reach the higher selectivity. The combination of the polymer membrane and inorganic membrane produce mixed matrix membranes (Aroon *et al.,* 2010). However, membrane separation research worldwide is still concerned to the development of the membranes due to the problem to obtain the higher selectivity and permeability (Iqbal, 2010). This view supported by the studies on the past three decades to increase the performance of gas separation membranes. This is because of some factors such as fabrication of mixed matrix membranes, particle size, particle pore size, dispersed phase load and polymer type and properties.

From the previous research, in MMMs fabrication, the most important criteria to be achieved are to ensure a good contact between polymer matrix and polymer sieves particles (Ismail *et al*., 2008). However, the successes mixed matrix membrane were obtained using various techniques to modify the preparation and formation protocol of the glassy polymer-sieve MMMs. Attempt was done by Ismail et al. through the addition of N-methyl-2-pyrrolidone(20wt%NMP) and zeolite 5A(30wt%) to formed a homogeneous solution. Then the polymer polyethersulfone (50%wt PES) was adding to the solution and this is by using first method dope solution preparation that will study future in this research. They found that, on annealed at above Tg (270°C), the selectivity of O_2/N_2 is increase to 4.5 and the permeability is decrease to 5.9. Another work done by Ahn *et al*. through the dissolved of polymer and solvent to formed a homogeneous solution and then adding the silica as a inorganic filler into the solution as follow second method of fabrication in this research. They found that, the selectivity and permeability increase. From the result mentioned above, it can be conclude that different methods dope solution preparation will give the different performance of mixed matrix membrane.

1.1 Problem Statement

There are a lot of gas separation technology develop in the recent year. One of them is membrane gas separation. The difficulties in the development of gas separation membranes are to achieve higher performance and higher selectivity. They are used the new alternative which is able to overcome the problem which are mixed matrix membranes (MMMs) (Aroon *et al.,* 2010). The previous research reported that in the development of Polyethersulfone MMMs, there are a lot of factors that affect the performance of gas separation such as weak contact of particles in the polymer matrix and poor distribution of dispersed phase in the continuous polymer matrix phase (Aroon *et al.,* 2010). The problem always occurs during the preparation of dope solution. Moreover, the study is limited for one type of preparation of dope solution. Therefore, this study will focus to find the best method with the higher performance for selectivity and permeability of polyethersulfone MMMs by comparing between three different methods.

1.2 Objective of the Study

To study the effect of different methods preparation of dope solution in the development of PES MMMs for O_2/N_2 gas separation by identified and analyzing their performance.

1.3 Scopes of the Study

There are several scopes related to this research which are:

a) Preparation of polymer solution using three different methods which are
   - i) First method, homogeneous suspension solution formation.
   - ii) Second method, homogeneous polymeric solution formation.
   - iii) Third method, combining homogeneous suspension with homogeneous polymeric solution.

b) Comparing the performance of develop coated membrane produced using three different method using O_2/N_2 gases.

c) Characterize the membranes morphology by using Scanning Electron Microscopy (SEM).

1.4 Rationale and Significance

It has been shown that, the higher selectivity of membrane is the goal of membrane separation process (Baker, 2000). Thus, the best method preparation of dope solution is important in the development of PES MMMs performance. The different methods will give the different result where the selectivity and the permeability of the membranes will be different. Therefore, this research must be done to find the effect of different method and the characteristic for each of the membranes. The better distribution of inorganic particles (zeolites) in the polymer solution will increase the selectivity of the gas separation. Thus, to overcome the challenges, this research should be done on the development of PES MMMs performance, with different method preparation of dope solution to have a higher potential to achieve high selectivity without decrease the permeability of gas.

CHAPTER 2

LITERATURE REVIEW

2.1 Membranes Separation Technology

In 1892, the foundation for gas separation was laid by Thomas Graham, who performed the first experiment on the transport of gases and vapors in polymeric membranes. Thomas Graham and Fick concepts in 1860s have contributed to the understanding of gas-diffusion phenomena (Pandey and Chauhan, 2001). Through the nineteenth and early twentieth centuries, there had no industrial and commercial uses of membranes, but only used as laboratory tools to develop physical or chemical theories (Baker, 2000). The progress in membrane separation technology was accelerated during 1980s. In this century, membranes gas separation was emerged as a commercial process on a large scale. In this period, significant progress was made in every aspect of membrane technology, including improvements in membrane formation processes such as interfacial polymerization and multiplayer composite casting and coating, chemical and physical structures, configuration and applications.

Membrane separation technology development of membranes provides many advantages especially in industrial applications. The gas separation membranes are applied to various field, as summarized in Table 2.1.

Table 2.1 : Application of Membrane Separation (Li *et al.,* 2008; Ravanchi *et al.,* 2009)

Object	Application
H_2	Refinery of petroleum : recovery of H_2 Chemical industry : control the balance of H_2 / CO, Recovery of H_2, produce of high purity H_2 Recovery of He from natural gas
CO_2	Remove acid gas from natural gas CO_2 separation from landfill gas
O_2 / N_2	Prevention discharge : piping, seal tank, transportation of powder, tanker of LPG, equipment of washing Prevention for oxidization : molding resin, laser cutting, disorder process Food : prevention for oxidization, preservation and transportation of perishable foods Medicines : prevention of oxidization Metal : prevention of oxidization
H_2/CO	Syngas ratio adjustment
H_2/N_2	Ammonia purge gas
H_2S/Hydrocarbon	Sour gas treating
H_2O/Hydrocarbon	Natural gas dehydration
H_2O/air	Air dehydration
Hydrocarbon/Air	Pollution control, hydrocarbon recovery
Dehydration	Dehydration of organic solvent

2.2 Concept of Membrane Separation Process

The differential mechanisms may be involved in transport of gases across a porous membrane (Pandey and Chauhan, 2001) and the solution-diffusion model (Baker, 2000). The mechanism for permeation of gases through porous membranes and solution-diffusion membranes are shown in Figure 2.1.

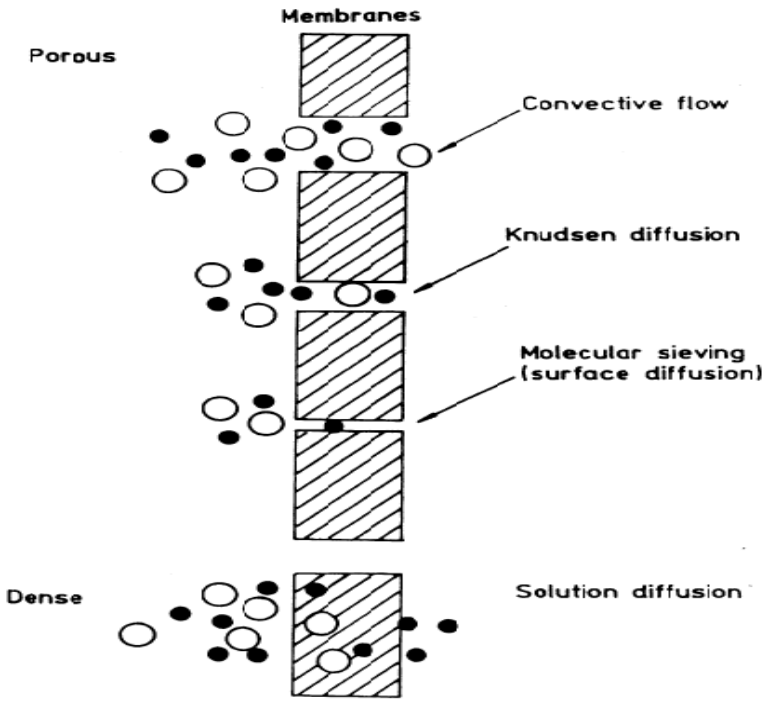

Figure 2.1: Schematic presentations of mechanisms for permeation of gases through membranes (Pandey and Chauhan, 2001).

Membrane permeate was the portion of fluid that has passed through the membrane whereas the concentrate steams contains the constituents that have been rejected by the membranes. The different gases pass through the membrane with the different rates. So that is permeating a partial separation. The components that diffuse more rapidly become enriched while the slower components are concentrated in the residue (Baker, 2000). The basic membrane gas separation process is illustrated as Figure 2.2.

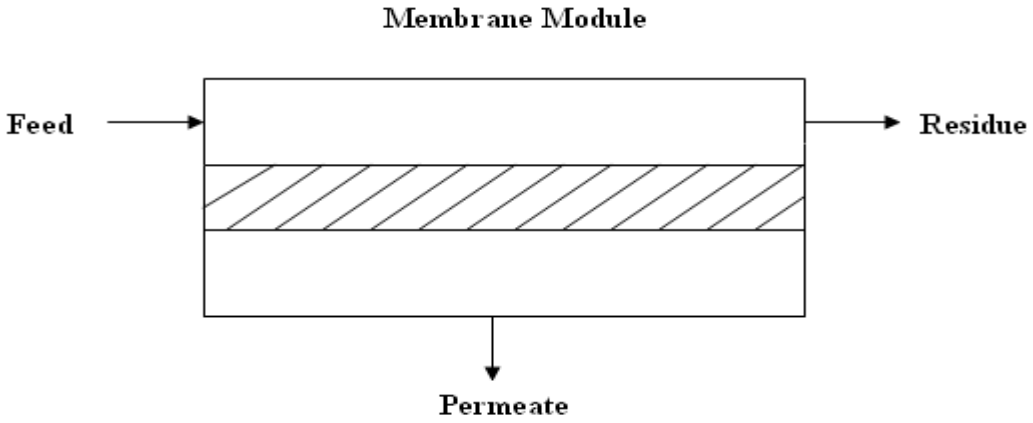

Figure 2.2: Schematic diagram of basic membrane for gas separation (Baker, 2000)

2.2.1 Asymmetric membranes

Membranes can be divided into two different structures namely as symmetric and asymmetric. Figure 2.3 and 2.4 illustrate the symmetric and asymmetric mixed matrix membrane. The functional of the membrane will depend on its structure and it is slightly different in term of physical and chemical properties. However, the symmetric membrane is significantly low permeability and they are hardly applied to practical uses thereby (Li *et al.,* 2008). So in order to achieve a higher permeability of the membrane, the asymmetric membrane will be use.

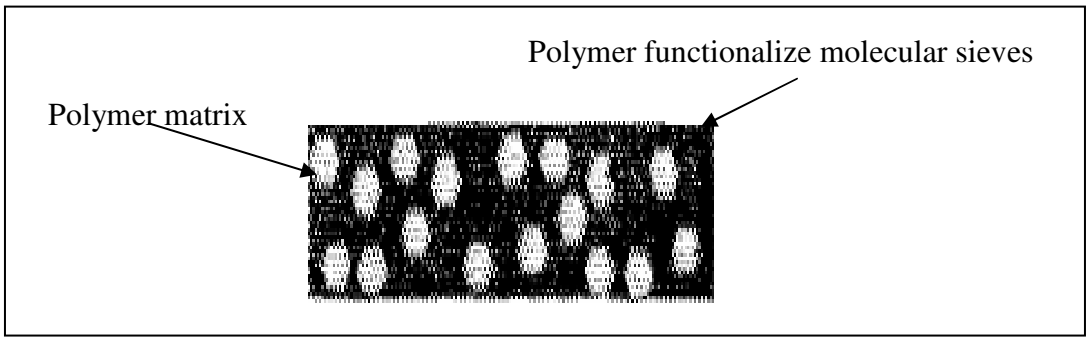

Figure 2.3: Schematic diagram for Symmetric Mixed Matrix Membrane (Liu *et al.,* 2009)

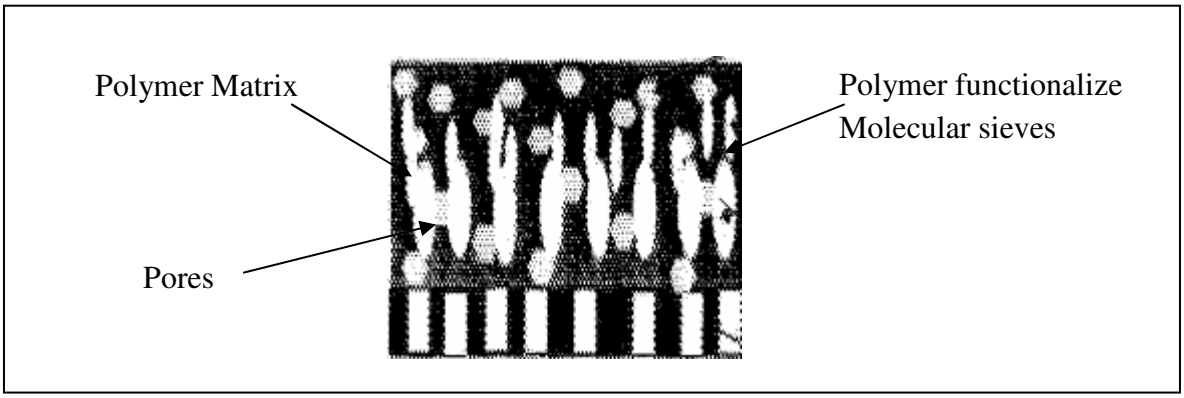

Figure 2.4: Schematic diagram for Asymmetric Mixed Matrix Membrane (Liu *et al*., 2009)

The asymmetric membrane is produced by Loeb and Sourirajan (1962) namely the dry or wet method. This is a process changing a one-phase casting solution into two separate phases (Baker, 2000). This method comprised of some steps which are preparing the dope solution, casting of the dope, coagulation process and drying of the coagulated membranes. The two phases consist of a solid, polymer rich phase and a liquid, polymer poor phase. The dry or wet phase inversion has been used to form defect-free asymmetric membranes from variety of glassy polymer (Ismail *et al*, 2003). The dry or wet inversion requires of multicomponent casting solution consist of volatile solvent and less volatile non -solvent. All of the solvent and non-solvent was immersed into coagulation bath while adding the non-solvent until the solution nears its phase boundary.

2.3 Mixed Matrix Membranes (MMMs) for Gas Separation

2.3.1 Concept of Mixed Matrix Membranes (MMMs)

In 1990, an upper limit was predicted by Roberson for the performance of polymeric membranes in gas separation (Roberson, 1991). In the polymeric materials, there exists a general trade off between permeability and selectivity with an upper-bound (Chung *et al*., 2007). So, when the materials with separation properties were near this limit, they were modified based on structure property relation and also the selectivity and permeability of the polymers.

The latest alternative approach is mixed matrix membranes (MMMs) which is involve in the latest membrane morphology emerging with the potential for future applications. As a new alternative, MMMs have a potential to obtain higher selectivity and permeability or both by addition of organic particles with their inherent superior separation characteristic, while maintaining their advantages such as low cost and easy process ability.

Mixed matrix membranes (MMMs) is a new hybrid membrane containing inorganic fillers such as molecular sieves dispersed in a polymer matrix. Based on the need for a more efficient membrane than polymer and inorganic membrane, MMMs are used as an alternative approach in membrane technology where gas separation properties of molecular sieve materials combine with desirable mechanical properties (Aroon *et al.,* 2010). Figure 2.5 and Figure 2.6 illustrated schematic diagram for mixed matrix membrane and the schematic diagram for three phases mixed matrix membrane system.

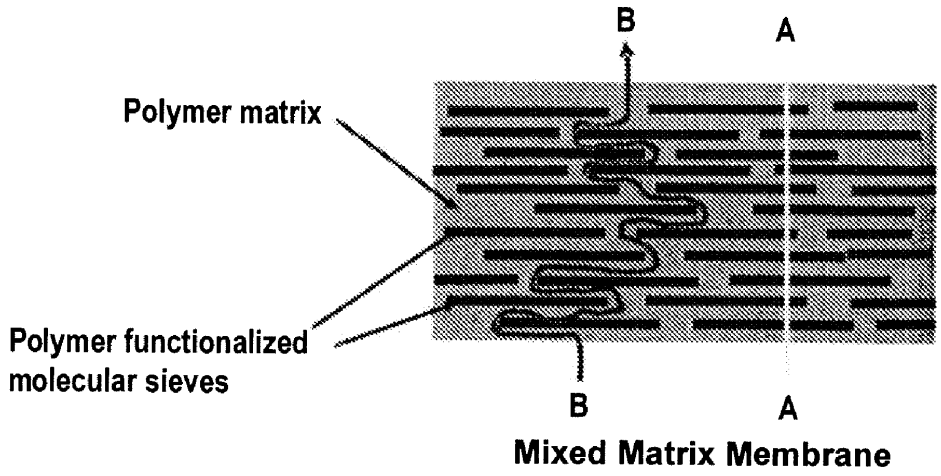

Figure 2.5: Schematic diagram for Mixed Matrix Membrane (Liu *et al.,* 2009)

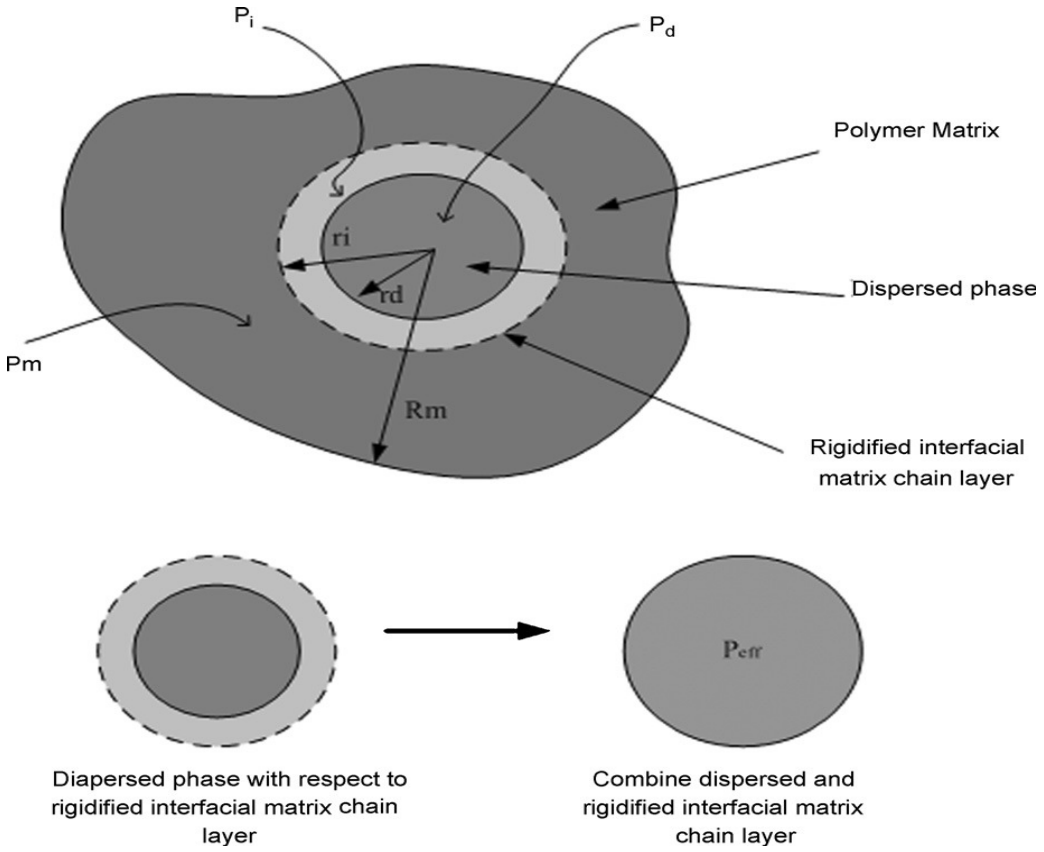

Figure 2.6: Schematic representation of three phases mixed matrix membrane system (Shimekit *et al.,* 2011)

Figure 2.6 above illustrate the separation mechanism of molecular sieve and polymer mixed matrix membranes combining solution-diffusion mechanism of polymer membranes and molecular sieving mechanism of molecular sieve membranes. The molecular sieves dispersed in the concentrated suspension are functionalized by a suitable polymer such as polyethersulfone (PES). The chain between polymer and molecular sieves particles results in the formation of either polymer-O-molecular sieve covalent bonds (Liu *et al*., 2009).

The mixed matrix membranes (MMMs) fabricated using the present approach combining the solution-diffusion mechanism of polymer membrane and the molecular sieving and sorption mechanism of molecular sieves results maximum selectivity and

consistent performance among different samples comprising the same molecular sieve and polymer composition (Liu *et al.,* 2009)

2.3.2 Molecular Design of Mixed Matrix Membranes (MMMs)

The recent research much focuses on the addition of porous particles into polymer matrices. The interaction between small volumes of inorganic fillers into polymer matrix can result increasing of separation efficiency. This situation predicted by Maxwell model. Maxwell model was developed in 1970s with the equation shown in equation 2.4. (Baker, 2000; Chung *et al*., 2007)

$$Peff = Pc\frac{(Pd + 2Pc - 2\emptyset(Pc - Pd))}{(Pd + 2Pc + \emptyset(Pc - Pd))} \tag{2.4}$$

Where P_{eff} the effective permeability of the mixed matrix material, Φ is is the volume fraction of the dispersed zeolite phase, Pc is the permeability of the continuous polymer phase and Pd is the permeability of the dispersed zeolite phase. If the equation is used to calculate the permeability of the mixed matrix membrane, the equation to be used to calculate the selectivity is as equation 2.5.

$$\alpha eff = \alpha c\frac{1 + 2Prel - 2\emptyset(Prel - 1)}{1 + 2Prel + \emptyset(Prel - 1)} * \frac{\frac{1}{\alpha D} + \frac{2Prel}{\alpha c} + \emptyset(\frac{Prel}{\alpha c} - \frac{1}{\alpha D})}{\frac{1}{\alpha D} + \frac{2Prel}{\alpha c} - 2\emptyset(\frac{Prel}{\alpha c} - \frac{1}{\alpha D})} \tag{2.5}$$

Where α is the effective selectivity, αc and αd is the selectivity of the continuous and dispersed polymer phase, P is the permeability. The indices 1 and 2 are referring to gas 1 and 2.

The dispersed and continuous phases should properly choose by taking transport mechanisms through membrane. When smaller component pass through, it will be more sensible when combined size selection of the inorganic fillers with molecular sieving characteristics and polymers based (Chung *et al.,* 2007).

2.4 Fabrication of Mixed Matrix Membranes (MMMs)

While the polymer upper-bond curve has been surpassed using hybrid membranes between inorganic fillers and polymer matrix, there are still many issues towards the fabrication for large scale industrial production of these new types of MMMs. Voids and defects interface for inorganic molecular sieves and the organic polymer matrix are reported in the literature (Liu *et al.,* 2009).

Fabricating an ideal mixed matrix with no defects in the polymer–particle interface is very difficult. Formation of the defects at the polymer–inorganic interface will result due to the weakness of polymer–particle adhesion because of the difference between the polymer and inorganic phase properties and the strong aggregation tendency of the fillers and poor distribution of the inorganic phase in the polymer matrix (Aroon *et al*., 2010; Liu *et al.,* 2009).

The performance of MMMs is reviewed and the applicable methods to fabricate a defect-free MMMs. The method of the fabrication of MMMs differs with each other based on the compatibility of the solution bonding. The important step of MMMs fabrication is preparing a homogeneous of polymer-inorganic particles. There are three methods can be used for MMMs fabrication as list in Table 2.2. The performance of the different methods of MMMs fabrication is reviewed in this study.